VAPOUR–LIQUID EQUILIBRIUM IN THE BINARY SYSTEMS FORMED BY ETHYLENE GLYCOL, DIETHYLENE GLYCOL, AND N-METHYLPYRROLIDONE

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Dedicated to late Academician Eduard Hála.

Vapour–liquid equilibrium data are given for the binary systems ethylene glycol (EG)–N-methyl-pyrrolidone (NMP), ethylene glycol–diethylene glycol (DEG), and N-methylpyrrolidone–di-ethylene glycol at 50°C. The measurement of vapour–liquid equilibrium was carried out in a modified version of semimicrostill from foregoing paper. This still makes it possible to measure even at the pressures of the order 10^1 Pa. The dependence of the excess Gibbs energy on composition was expressed by the 4th order Redlich–Kister, Wilson, and NRTL equations. The systems EG–NMP and DEG–NMP exhibit negative deviations from ideal behaviour, EG with DEG form practically ideal solution.

NMP in combination with EG or with higher glycols is a widely used mixed solvent in chemical industry for the extraction of aromatic hydrocarbons from petrol fractions. Mixed solvents are noted for low vapour pressures at working temperatures. Therefore, the common circulation and static methods, survey of which was given by Hála[1] and Aim[2], are not suitable for obtaining the vapour–liquid equilibrium data of these systems. The experimental data needed for thermodynamic treatment of the above-mentioned mixed solvents are not practically available in open literature, and they even cannot be calculated in terms of some contribution methods, such as UNIFAC[3].

Experimental vapour–liquid equilibrium data are given in this paper for the binary systems NMP–EG, NMP–DEG, and EG–DEG at 50°C measured in the modified semimicrostill.

Surový and coworkers[4] proposed a comparatively simple differential method for measuring vapour–liquid equilibrium suitable for the measurements at pressures around 100 Pa. The use of the semimicrostill for binary systems whose pressure was substantially lower than 100 Pa (EG, DEG) was not suitable. The real time of measuring was considerably extended and the possibility of occurring the partial condensation was not eliminated either. The modified semimicrostill published in this

work eliminates these phenomena and makes it possible to measure even at pressures of the order 10^1 Pa. From the comparison of remeasured equilibrium data of the NMP–EG system with those published[4], it is evident that the mole fractions in the vapour phase $2-3\%$ lower were obtained on using the modified version of semi-microstill. The differences are probably due to the partial condensation in the older type of apparatus.

EXPERIMENTAL

Modified Semimicrostill for Measuring the Vapour–Liquid Equilibria at Low Pressures

The modified semimicrostill works isothermally on the principle of differential distillation and stems from the same theoretical considerations as the original version of semimicrostill[4]. It is noted for some design changes which considerably facilitate the vapour–liquid equilibrium measurement (especially in systems whose vapour pressure is substantially lower than 100 Pa), control the real time consumption in measurement and eliminate the vapour partial condensation.

The outline of the modified semimicrostill is in Fig. 1. The still is of relatively simple design. It consists of equilibrium flask A whose mildly elongated arm is bent and connected to vacuum G via two-way vacuum cock C. The flask is equipped with ground-in stopper D for feeding or taking the liquid samples. The thorough stirring of the liquid is ensured by magnetic stirrer F. Unlike the original type, the place of sampling the vapour phase is shifted to the tempered part of the semimicrostill. Distilling tube H for interchangeable receiver B is in its upper part considerably extended to prevent the formation of so-called "air plugs". The isothermal regime is maintained in the distillation flask by means of fixed tempering jacket I, and the heating of the receiver by portable tempering jacket E. The pressure in the system is monitored with a Pirani gauge. In the vacuum part outside the two-way vacuum cock, a set of exchangeable capillaries K of various inner diameters is placed. On using them, the rate of evacuating and in this way also the real time consumption in measuring various systems are controlled. For example, for the NMP–EG system with higher NMP content, the capillary of 1 mm i.d. and about 10 cm long
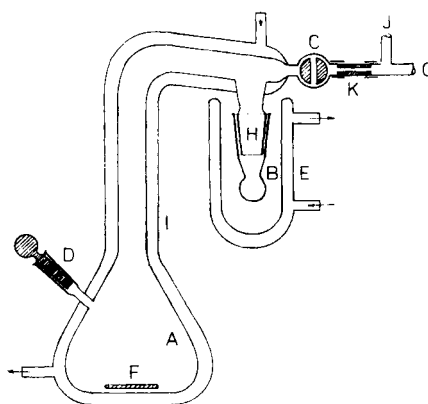

FIG. 1

Modified semimicrostill for measuring vapour–liquid equilibrium at low pressures. A Equilibrium vessel, B exchangeable receiver, C vacuum cock, D opening with ground-in stopper, E portable tempering jacket, F magnetic stirrer, G connection to vacuum through a capillary, H distilling tube for exchangeable receiver, I fixed tempering jacket, J connection to Pirani gauge, K capillary

proved to be adequate in our arrangement, whereas in case of the EG–DEG system it is not necessary to use capillary at all.

Despite the measurement takes place in non-stationary mode, the results of measurements may be evaluated in most cases as results of stationary measurement. The error due to the un-stationary operation of the still was studied in our foregoing work[4].

Vapour–Liquid Equilibrium Data Measurement

The liquid mixture is transferred into the equilibrium flask A through the opening D. The still is closed, and the sample is heated up to the required temperature on being stirred all the time regularly. The system is let to be tempered for a sufficiently long time period (1—2 hours). After having been tempered, the flask is evacuated and at the same time, a part of exchangeable receiver is intensively cooled with a cooling mixture (mixture of acetone and solid CO_2). In this cooled part of receiver, the condensation of the equilibrium vapour phase takes place. After the condensation of $0.1—0.2$ cm^3 sample, the system is aerated, and the samples of both phases are taken for chromatographic analysis. The optimum condensation time (10—20 min) can be achieved by a suitable selection of the capillary with respect to the solution volatility, partly by interrupting the evacuation of the still in different time intervals.

Vapour–liquid equilibrium of the binary systems NMP–EG, NMP–DEG, and EG–DEG was determined at the temperature of $50 \pm 0.1°C$, the pressure value in the vacuum part was about 5 Pa, in the still $10^1 — 10^2$ Pa. The chromatographic analysis was carried out using a packed column filled with stationary phase 10% neopentyl glycol succinate on a support. The column temperature was 160°C. The accuracy of the chromatographic analysis was higher than ± 0.5 mole %.

The EG used was prepared from EG, A.R. grade (Loba Chemie, Wien) by using vacuum rectification in a column with efficiency about 10 theoretical plates. The product was dried with molecular sieves. NMP and DEG were prepared from technical products used in Slovnaft, Bratislava, by twofold vacuum rectification in a column with efficiency about 10 theoretical plates and by drying with molecular sieves. The chemicals used had chromatographic purity higher than 99.8%

RESULTS

The measured isothermal $y–x$ equilibrium data at 50°C of the systems NMP–EG, NMP–DEG, and EG–DEG are given in Table I and graphically plotted in the form of $y–x$ equilibrium diagrams (Fig. 2). It is apparent that the systems NMP–EG and NMP–DEG exhibit negative deviations from ideal behaviour. The EG–DEG system approaches ideal behaviour.

The experimental equilibrium data of the NMP–EG system were compared with the set of experimental data published in our preceding paper[4]. As it is evident from Fig. 2, the sets of experimental data differ. The remeasured $y–x$ equilibrium curve shows less convex shape, the obtained mole fractions in the vapour phase being $1 — 2.5$ mole % lower. The differences are assumed to be caused above all by partial condensation which could take place in the original semimicrostill owing to its design. In the new still, the partial condensation is practically beyond consideration.

The sets of experimental data were correlated by the 4th order Redlich–Kister equation

$$G^E/RT = x_i x_j \left[B_{ij} + C_{ij}(x_i - x_j) + D_{ij}(x_i - x_j)^2 \right], \qquad (1)$$

TABLE I

Experimental equilibrium data of the binary systems studied ($t = 50°C$)

| NMP–EG		NMP–DEG		EG–DEG	
x_{NMP}	y_{NMP}	x_{NMP}	y_{NMP}	x_{EG}	y_{EG}
0·048	0·077	0·016	0·237	0·030	0·303
0·090	0·151	0·028	0·392	0·060	0·443
0·134	0·197	0·041	0·500	0·084	0·517
0·170	0·253	0·059	0·601	0·110	0·604
0·226	0·330	0·097	0·748	0·234	0·795
0·271	0·391	0·139	0·811	0·278	0·824
0·312	0·444	0·182	0·836	0·465	0·898
0·376	0·536	0·218	0·898	0·556	0·928
0·411	0·582	0·259	0·917	0·598	0·939
0·469	0·641	0·319	0·931	0·698	0·957
0·502	0·700	0·422	0·964	0·785	0·977
0·563	0·778	0·514	0·972	0·887	0·98
0·643	0·841	0·580	0·975		
0·688	0·876	0·696	0·985		
0·816	0·945	0·773	0·992		
0·916	0·980	0·865	1·000		
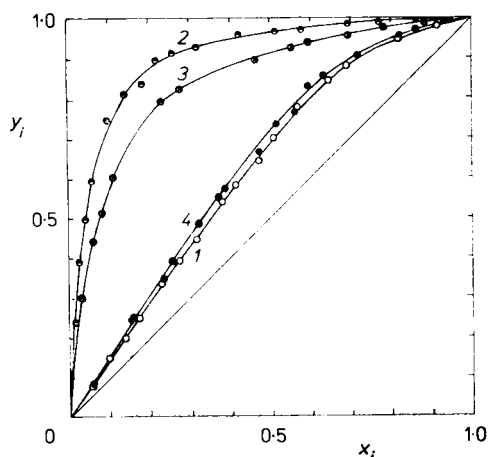
FIG. 2

Calculated y–x curves of the systems studied ($t = 50°C$). 1 NMP–EG, 2 NMP–DEG, 3 EG–DEG, 4 NMP–EG published[4]; the circles are experimental points of the above-mentioned systems

the NRTL equation

$$G^{E}/RT = x_i x_j \tau_{ji} \exp\left(-\alpha_{ij}\tau_{ji}\right)/\left[x_i + x_j \exp\left(-\alpha_{ij}\tau_{ji}\right)\right] +$$
$$+ x_i x_j \tau_{ij} \exp\left(-\alpha_{ij}\tau_{ij}\right)/\left[x_i \exp\left(-\alpha_{ij}\tau_{ij}\right) + x_j\right] , \qquad (2)$$

and the Wilson equation

$$G^{E}/RT = -x_i \ln\left(x_i + x_j \Lambda_{ij}\right) - x_j \ln\left(x_j + x_i \Lambda_{ji}\right) . \qquad (3)$$

TABLE II

Values of parameters of the NRTL, Wilson, and Redlich–Kister equations, mean and standard deviations in mole fractions of the binary systems at $t = 50°C$

Parameter	Binary system		
	NMP–EG	NMP–DEG	EG–DEG
NRTL equation			
α_{ij}	0·60	—0·4794	0·4365
τ_{ij}	0·3114	0·6374	—0·7573
τ_{ji}	—0·8143	—1·2706	1·1669
$d_x . 10^3$	3·12	2·13	2·32
$d_y . 10^3$	2·90	2·94	4·41
$\sigma_x . 10^3$	4·20	3·95	2·67
$\sigma_y . 10^3$	3·69	4·30	5·13
Wilson equation			
Λ_{ij}	2·4339	0·4844	0·3711
Λ_{ji}	0·6778	2·0244	1·9086
$d_x . 10^3$	3·25	2·26	2·05
$d_y . 10^3$	3·02	3·34	4·34
$\sigma_x . 10^3$	4·16	3·57	2·75
$\sigma_y . 10^3$	3·70	4·64	5·41
Redlich–Kister equation			
B_{ij}	—0·6554	—0·1596	—0·0545
C_{ij}	—0·1836	0·1379	—0·3399
D_{ij}	0·1967	—0·0902	—0·3029
$d_x . 10^3$	1·85	2·08	1·52
$d_y . 10^3$	1·51	2·94	1·98
$\sigma_x . 10^3$	2·94	3·92	2·38
$\sigma_y . 10^3$	2·39	4·29	2·64

$p^o_{EG} = 89·5$ Pa; $p^o_{DEG} = 7·3$ Pa

To evaluate the parameters of the equations, the computation procedure reported in paper[4], i.e., the minimization of the objective function

$$F = \sum_{m=1}^{M} \left[(y_i - y_{i,calc})^2 + (x_i - x_{i,calc})^2 \right]_m \tag{4}$$

was used. The calculation of $y_{i,calc}$ starts from the assumption of ideal behaviour of the vapour phase. With respect to the low value of pressure in the system (below 100 Pa), this assumption may be considered to be correct. Further calculated parameters are the incidental parameters $x_{i,calc}$ and the saturated vapour pressures of pure components (EG and DEG) at the experimental temperature.

The value of saturated vapour pressure of NMP was extrapolated from experimental data published by Aim[5]. $p^o_{NMP} = 224·5$ Pa. The saturated vapour pressures of EG and DEG occur as further parameters for the literature data of their values differ considerably[6–9]. However, the values of p^o_i were not optimized when processing the data in the EG–DEG system. In this case the values of p^o_i calculated on the basis of the 4th order Redlich–Kister equation from the experimental data of the NMP––EG system, i.e., $p^o_{EG} = 89·5$ Pa, and of the NMP–DEG system, i.e., $p^o_{DEG} = 7·3$ Pa, were used for calculating the equilibrium compositions.

The values of parameters of the above-mentioned correlation equations and the corresponding values of mean and standard deviations in mole fractions are given in Table II. The best agreement of the experimental and calculated data was achieved with the 4th order Redlich–Kister equation. The values of mean deviations in mole fractions are within $1·5–3·0 . 10^{-3}$, standard deviations within $2·4–4·3 . 10^{-3}$. It is evident from the table that the flexibility of the NRTL and Wilson equations is lower for the systems investigated. The values of mean deviations in mole fractions are for these two equations within $2·0–4·5 . 10^{-3}$, of standard deviations in mole fractions are within $2·5–5·5 . 10^{-3}$.

SYMBOLS

B, C, D	model parameters of 4th order Redlich–Kister equation
d	mean deviation
F	objective function
G^E	excess molar Gibbs energy
M	total number of measurements
p	(total) vapour pressure
R	gas constant
t	temperature (centigrade)
T	thermodynamic temperature
x	mole fraction in liquid
y	mole fraction in vapour
σ	standard deviation

α_{ij}, τ_{ij} model parameters of NRTL equation
Λ_{ij} model parameters of Wilson equation

Superscripts

o   pure component

Subscripts

i, j   designation of components (i more volatile component)
m   designation of experimental point

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